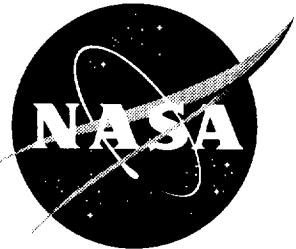


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Monte Carlo Simulation of Endlinking Oligomers

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Introduction

Crosslinked polymers fall into two classes: random networks, and networks produced by the endlinking of reactive oligomers. The former include such technologically important materials as vulcanized rubber and vinyl/di-vinyl copolymers. Members of the second class, produced via endlinking chemistries, are also of practical importance (RTV silicones, epoxy resins, solid propellant binders) and, in addition, have played a role in testing statistical theories of rubber elasticity [1, 2, 3].

In high-performance materials, the use of oligomers with reactive end groups helps processing and imparts solvent resistance -- even when the degree of crosslinking is quite small [4, 5]. A better understanding of the network structure in these materials will help in optimizing their performance.

This report describes initial efforts to model the endlinking reaction using a lattice Monte Carlo technique. Previous simulations of crosslinking ignored the space-filling quality of molecules to focus on reactions in complex mixtures [6], imposed arbitrary diffusion constants [7], or concentrated on network relaxation [8]. In the present study, the relatively efficient Bond Fluctuation Model [9] allows study of the effect of oligomer molecular weight at bulk densities [10] .

The Model

The Bond Fluctuation Method (BFM) in 3 dimensions [11] was implemented here on a $20 \times 20 \times 20$ unit lattice with periodic boundary conditions. Bulk density corresponds to 500 "mers" in the cell. The repeat units (mers) will be called simply "nodes", since each link in the model represents several actual chemical bonds [9]. Model chains of $n = 5, 10, 20$, and 40 nodes were studied. The chains were initially packed on the lattice in a regular array, then allowed to randomize before beginning the crosslinking

process. The “melt” was equilibrated for sufficient time for the center of mass of a chain to diffuse a distance equal to its root mean square end-to-end distance.

To simulate reactions, each time a chain end was moved, the adjacent lattice sites were checked for the presence of another end. If one was present in the allowed bond distance, the two ends were linked. Several different allowed distances were tried, as described in the results. Chain ends remained reactive throughout, so that multiple links were permitted. Even in two dimensions, up to eight connections are possible to a given node [9]. In three dimensions, 16 connections appear possible.

Results and Discussion

A. Simulations

An equilibrated “melt” of short chains ($n=5$) is depicted in Figures 1a and 1b. For the starting linear chains, every node has either one or two connections. Bonds which would have extended across the periodic boundary are not shown in the figure, which explains the unconnected nodes that appear near the edges of the cube. For purposes of illustration, the 200 reactive chain ends are rendered in a darker color. In the simulation, each node, whether chain end or interior, occupies one lattice site.

With Figure 1 as the initial configuration, the Monte Carlo simulation was restarted and new bonds were allowed to form at the chain ends according to the crosslinking rule. It is impossible to say *a priori* how many new bonds will form. In this respect, this simulation is different from previously published work in which the functionality and stoichiometry of the crosslinking reaction were assumed to be known. Because the functionality of the crosslinks is essentially unlimited, the network structure is controlled only by the chain connectivity and excluded volume interactions.

It is of interest to know how the bonding assumptions affect the course of the crosslinking “reactions”. The most restrictive assumption would be that reactive nodes react only when they collide. In the Bond Fluctuation Model, excluded volume constraints prevent actual collisions, but virtual collisions could be recorded if such a move was rejected in the course of the simulation. Only slightly less restrictive would be the assumption that a bond is formed whenever an eligible node moves to a site that is at the closest allowed distance to another eligible node. This is case (a) in Table I. Under this assumption, only six neighboring sites are close enough to allow bonding to any given node. (Note, however, that even if a bond is formed to one of these sites, the site is not blocked permanently, so the crosslink functionality can still be higher than 6 in principle).

The least restrictive prescription for crosslinking is to form a bond of any allowed length provided that it would not violate the rules that prevent chains from passing through each other. The latter restriction eliminates 48 of the 108 possible bond vectors. Thus a total of 60 neighboring sites allow bonding. This is case (d) in Table I. Cases (b) and (c) represent intermediate degrees of constraint on the crosslinking reaction. Each case was carried out from two different starting configurations, to give an idea of the repeatability of the calculations.

Table I
Maximum Degree of Crosslinking Under Various Assumptions

Case	Maximum Distance for Bond Formation	Number of Sites Considered	Total Bonds Formed
(a)	2	6	137 131
(b)	$\sqrt{5}$	30	145 141
(c)	$\sqrt{6}$	54	159 154
(d)	3	60	154 155

Note that the less restrictive assumptions lead to more and earlier crosslinking (Figure 2). Although a detailed examination of kinetics is outside the scope of the present study, we note that for practical purposes the reaction had stopped after 10^5 Monte Carlo steps. Continuing the simulation for an additional 7×10^5 steps produced no additional bonds. In modeling actual endlinking molecules, the choice among cases (a) through (d) would presumably be made based on knowledge of the chemistry involved. In the following, we focus attention on the restrictions arising from the longer-range connectivity by concentrating on networks created under assumption (d).

Figure 3 is a histogram of the observed end group functionalities. Eight chain ends out of the initial 200 remained unreacted, (functionality of 1) apparently due to their inability to reach other ends. The most probable functionality is 2, i.e., what would be regarded as “chain extension” rather than crosslinking. The largest functionality found was 5. The number-average crosslink functionality is given by

$1 + 2 \cdot (\text{number of bonds formed}) / (\text{initial \# chain ends})$. Thus the average functionality is $1 + 2 \cdot (155) / 200 = 2.55$. Figure 4 illustrates the functionalities obtained with longer chains, and Table II summarizes the results for a range of chain lengths.

Table II
Effect of Chain Length on Degree of Crosslinking

n	Number of Chains	Number of Unreacted Ends	Number of Nodes with Functionality of 3 or Greater	Number of Bonds Formed	Average Crosslinking Functionality
5	100	9	83	155	2.55
10	48	3	38	74	2.54
20	24	0	16	35	2.46
40	12	0	7	16	2.33

Figures 5a and 5b illustrate the final, crosslinked structure of a simulated assembly of moderately long chains.

B. Scaling

There are several characteristic length scales in the simulation. The first is the lattice unit, which determines the “monomer” excluded volume and the concentration of chain ends. Next is the end-to-end distance of the polymer chain, which can be related to a chain stiffness. Finally, there is the size of the periodic cell, which must be large enough to avoid artifacts arising from a chain’s interaction with its periodic image.

Paul and co-workers [12] assert that the lattice occupation used in the present study (close to 50%) corresponds to bulk conditions. Equating this to the bulk density of PETI-5, we obtain the result that the lattice spacing is equivalent to 0.33 nm. It follows that the concentration of chain ends is $2 \cdot (480 / n) / [(8000) \cdot (0.33)^3] = 3.48/n$ per nm³. In a real specimen of PETI-5, with a nominal number average molecular weight of 5000 g/mol, the concentration of ends is 0.32/nm³. Therefore, in this respect, n=10 is a reasonable representation of this material.

The mean-square chain end-to-end distance in the simulation at n=10 was about 80 (lattice units)², which scales to 8.7 nm². The estimated mean-square end-to-end distance [5] of PETI-5, on the other hand, is about 67 nm². Therefore, in order to represent PETI-5, it will be necessary to increase the chain stiffness. This can be done straightforwardly by biasing the Monte Carlo acceptance criterion toward larger bond angles.

C. Chemistry

In most of the present work, very lenient bonding criteria were imposed for the endlinking reaction. In doing this, the intent was to focus on the purely geometric effect of the network formation on the long-range mobility of the chains. What was discovered is that the reaction is self-limiting: crosslinks are fairly rare even though all chain ends remain active (capable of bonding) throughout the simulation.

A comparison with experiment must come through a measurement of the apparent number of elastically-active chains in the sense of rubber elasticity theory. It is assumed that for a strand to be elastically-active, it must be attached via both ends to nodes of functionality 3 or greater. The detailed percolation paths in the model networks were not analyzed, but in an average sense, the data in Table II imply that 39% of the chains would have a functionality higher than 2 at one end. Then the probability of a functionality higher than two at both ends is $(0.39)^2 = 0.16$. This

agrees very well with experiments on PETI-5, which showed that about 1/6 of the initial chains behaved as elastically-active strands [5].

If more were known about the crosslinking chemistry in PETI-5, that knowledge could readily be incorporated into the model. For example, initiation, propagation, and termination of end-group polymerization could be modeled by having a limited number of active sites, with activity jumping to new nodes as bonds are formed. As it happens, free-radical reactions occurring in the neighborhood of 370°C (the curing temperature of PETI-5) may be fairly non-specific. The role of oxygen is another unknown.

One additional refinement to the model would be to incorporate a more realistic distribution of chain lengths. Small unlinked chains should be very mobile, and may affect the topology of the network. An assembly with the most-probable distribution of molecular lengths could be produced in a preliminary Monte Carlo run in which bonds are created between monomers.

Conclusions

It was found that even under very liberal crosslinking assumptions, geometrical factors limit the degree of crosslinking in endlinking networks. Surprisingly, the average crosslink functionality does not depend much on the chain lengths. These results provide a partial explanation of the low degrees of crosslinking inferred from experiment in a cured phenylethynyl-terminated polyimide oligomer.

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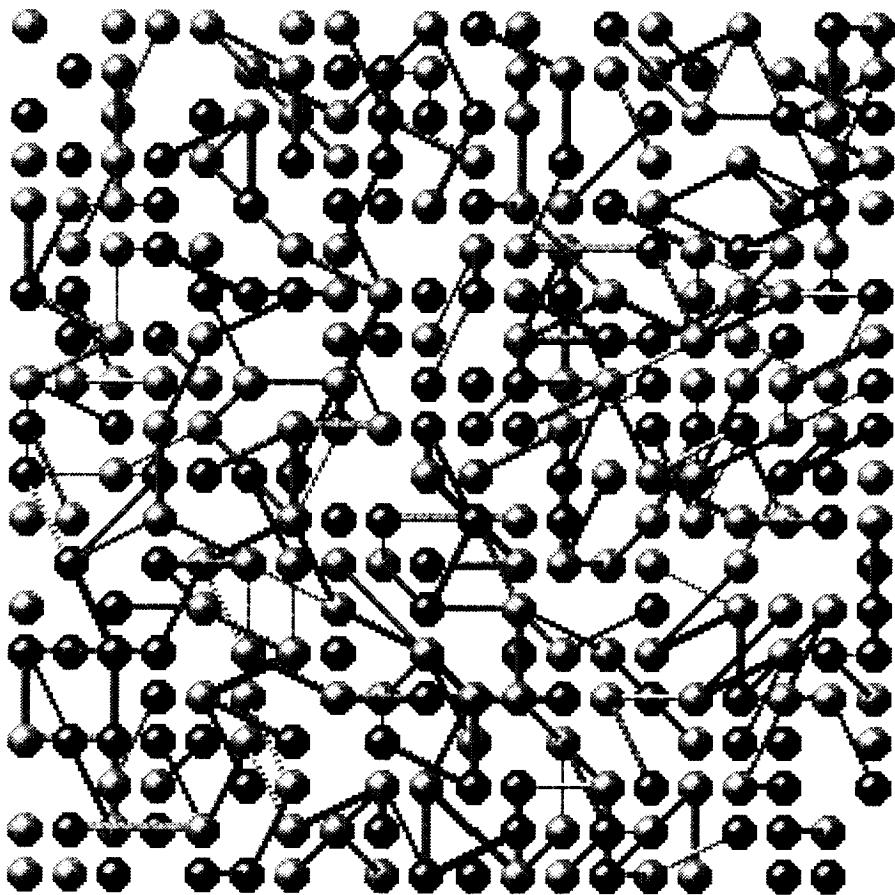


Figure 1a. Side view of lattice populated with linear chains ($n=5$). Each occupied lattice site is represented by a sphere of radius 0.4 lattice units. Darker spheres are chain ends.

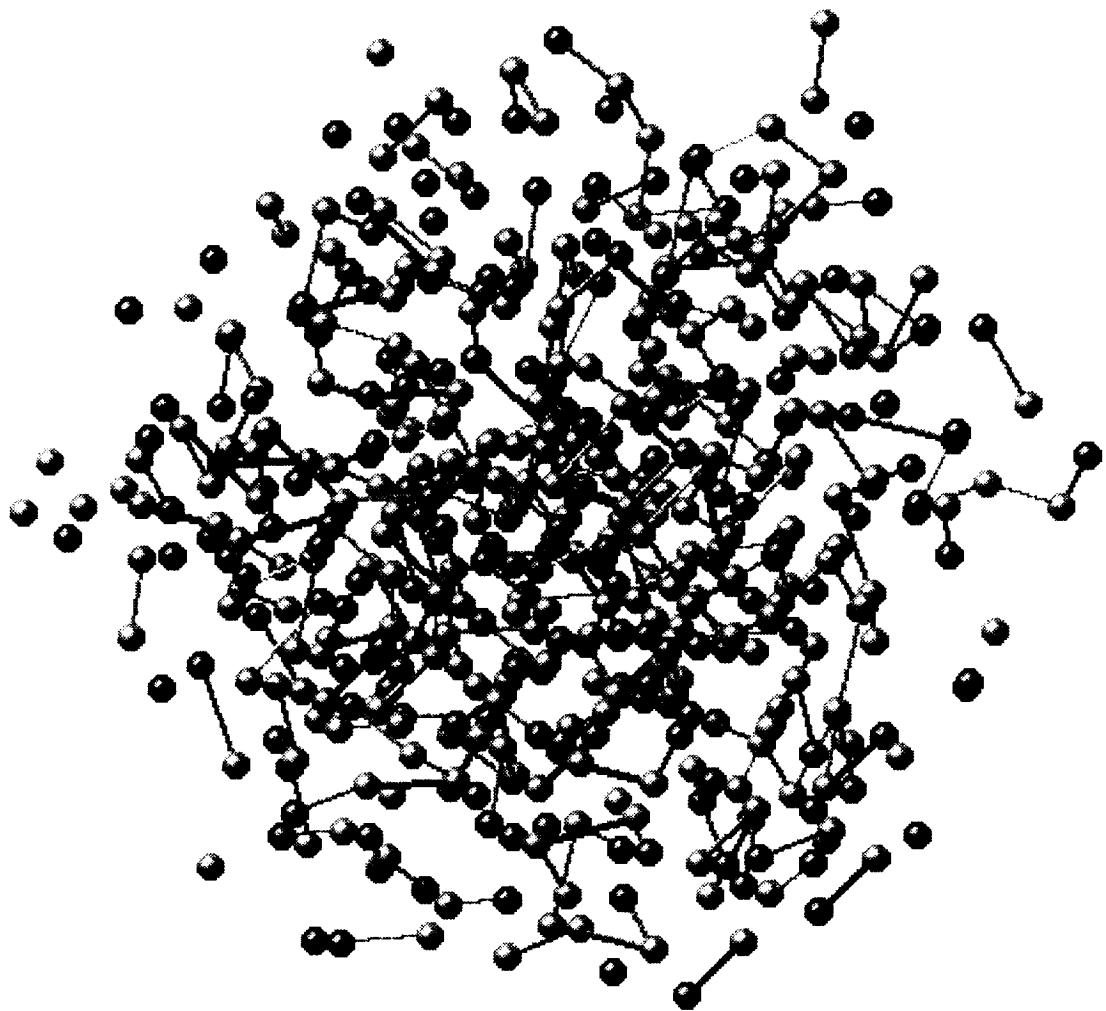


Figure 1b. Same structure as in Fig. 1a, but viewed from corner of periodic cell.

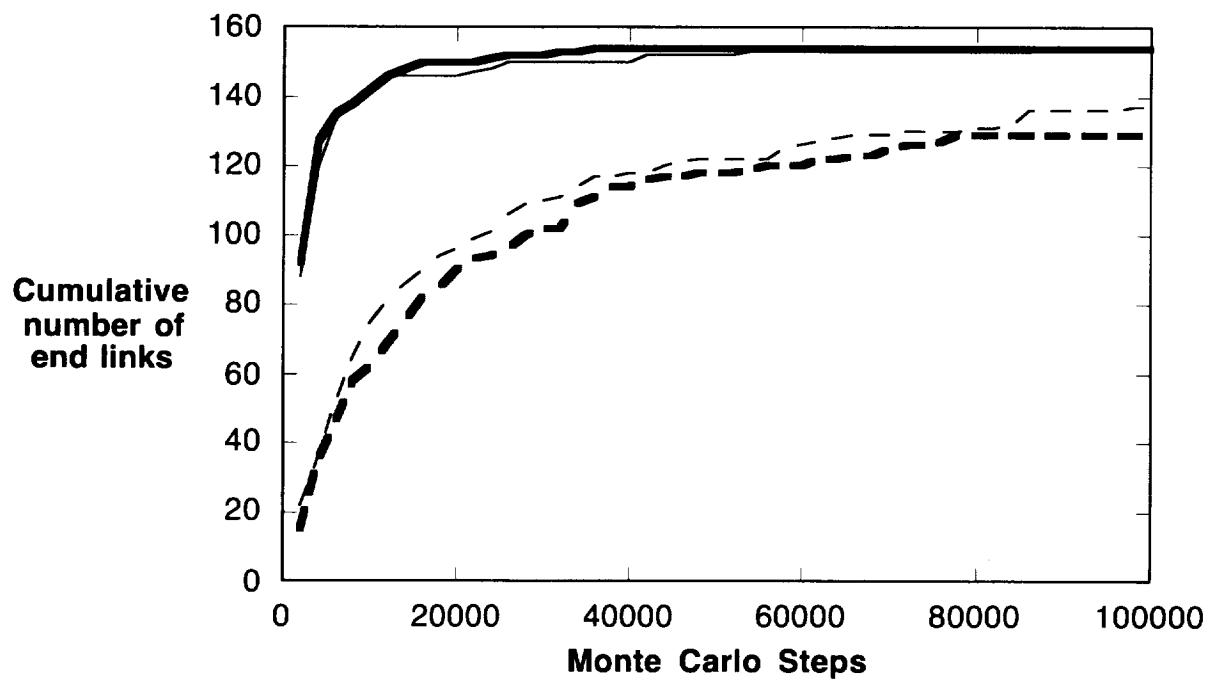


Figure 2. Course of endlinking reactions under two different assumptions. Dashed lines: case (a). Solid lines: case (d). Each case was run using two different initial configurations.

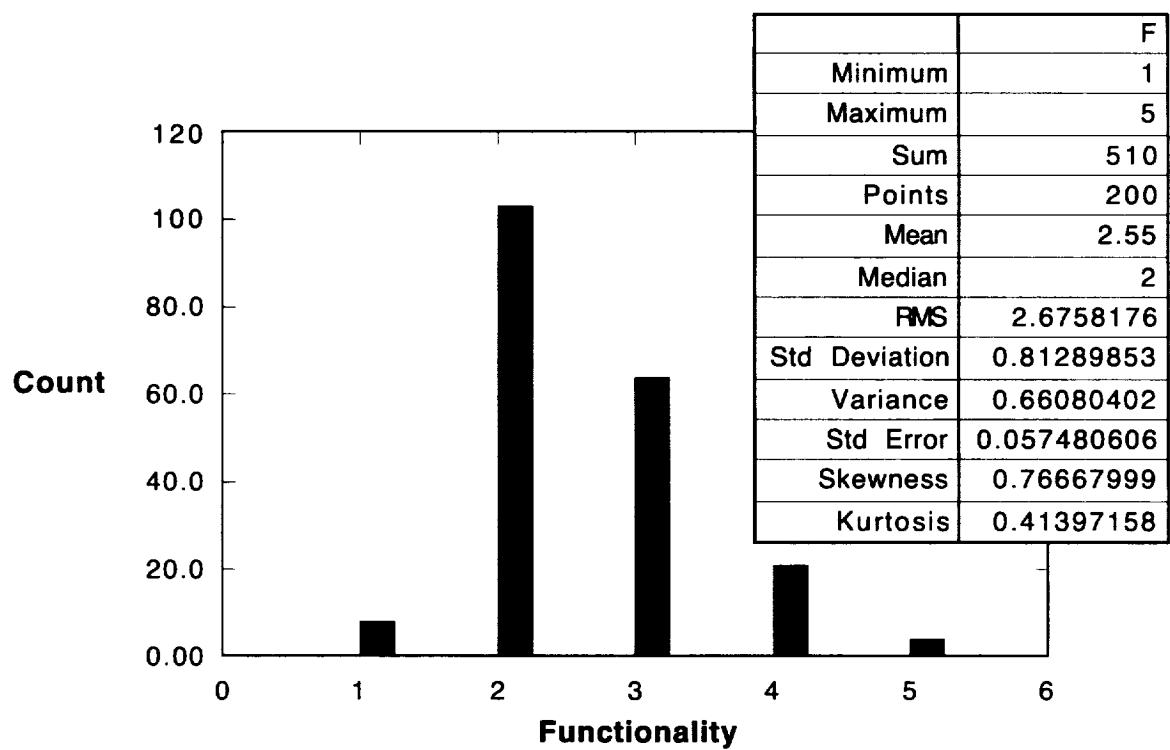


Figure 3. Histogram and summary statistics for crosslink functionality, $n=5$

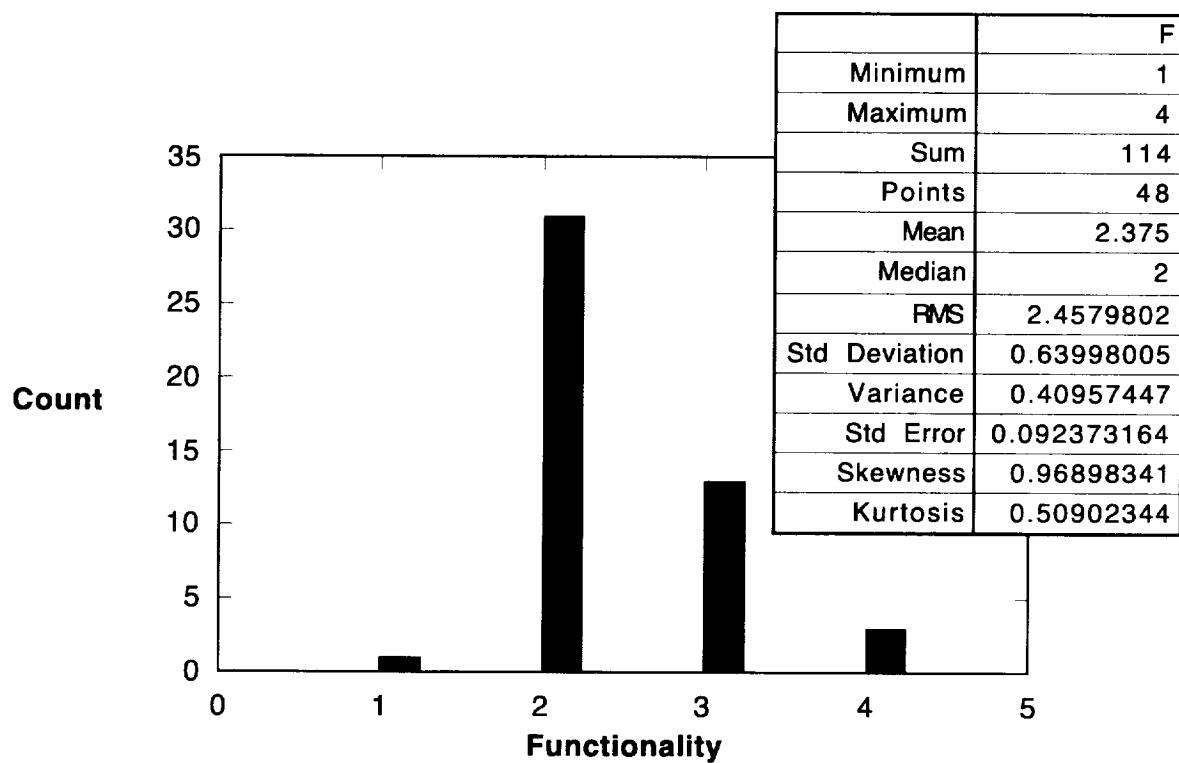


Figure 4. Histogram and summary statistics of final functionalities of 48 chain ends
($n=20$)

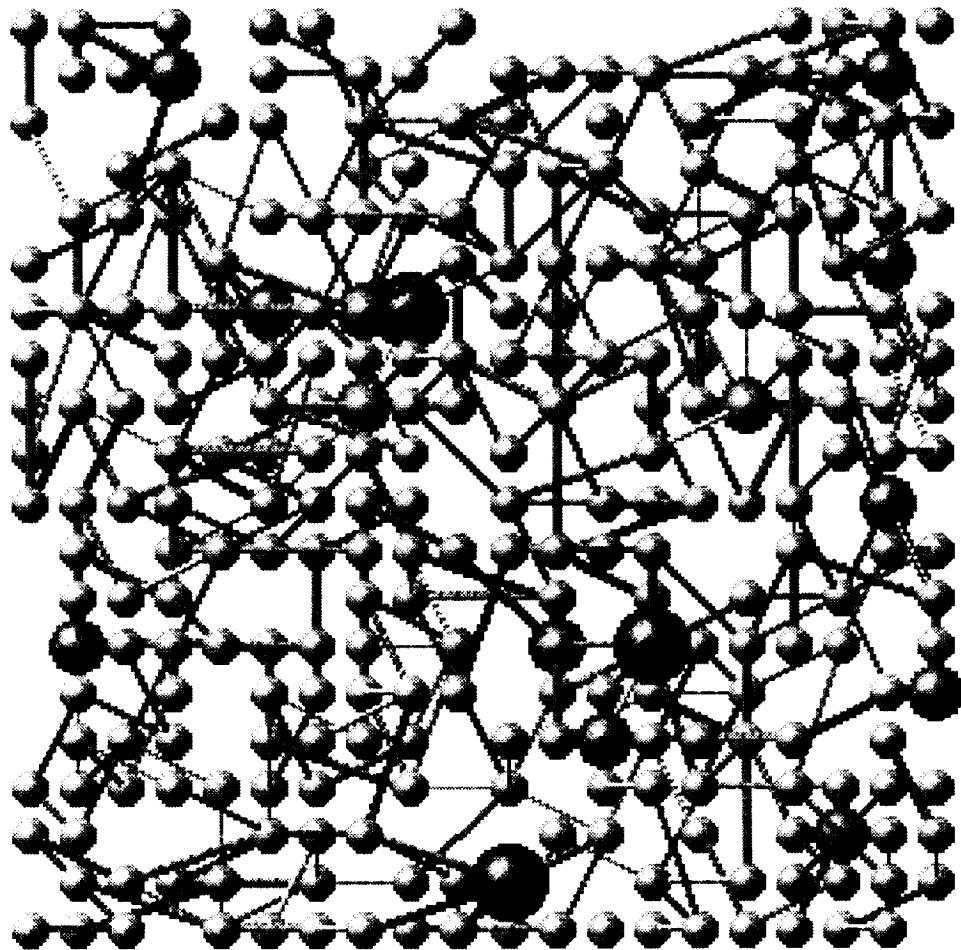


Figure 5a. Network structure obtained by crosslinking longer chains ($n=20$). An artificial display is generated by assigning larger sizes and darker colors to represent higher functionalities. For example, nodes with a functionality of 5 are shown as spheres of radius 1.0 lattice units. (in the actual simulation, all nodes are equivalent.)

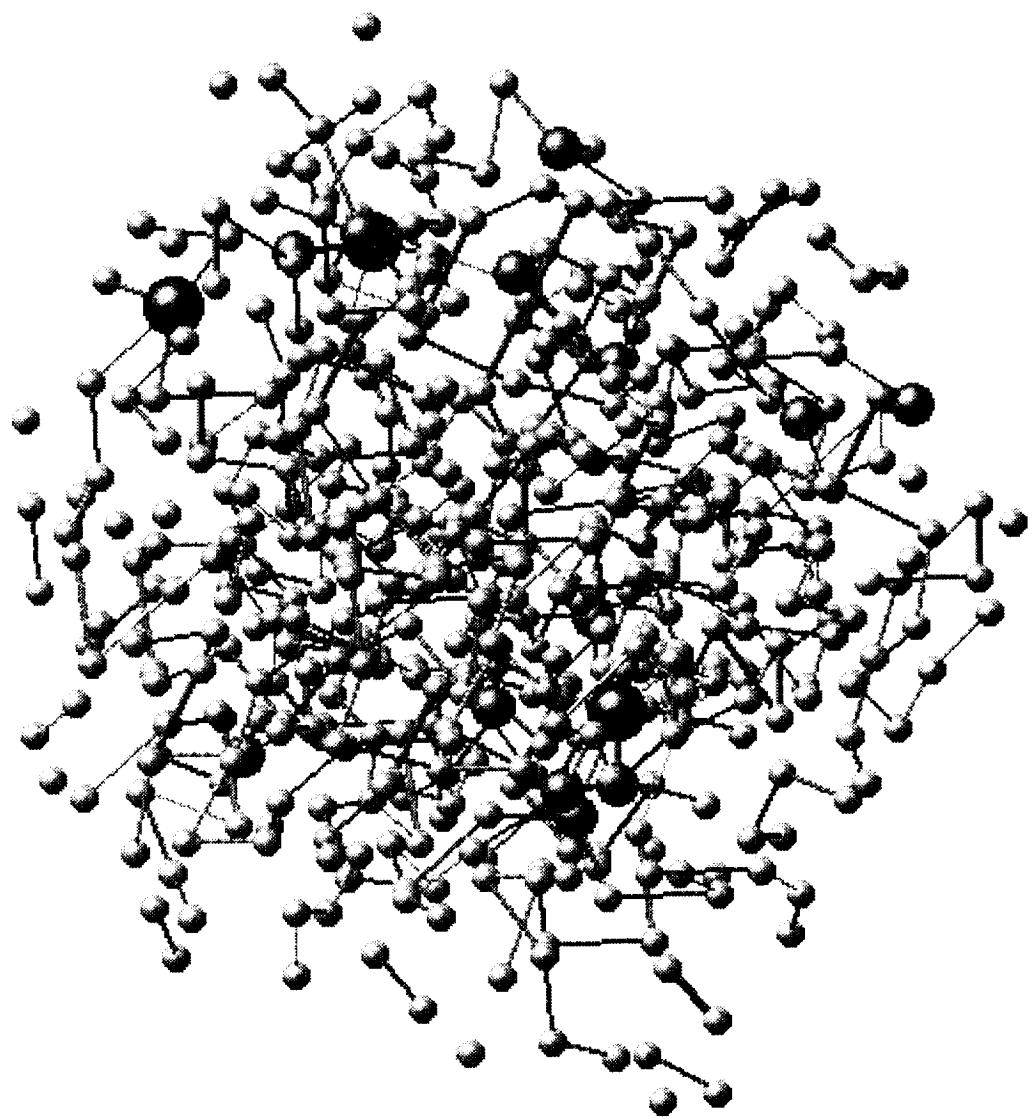


Figure 5b. Same structure as Figure 5a, but viewed from corner of cube.

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13. ABSTRACT (Maximum 200 words) This report describes initial efforts to model the endlinking reaction of phenylethynyl-terminated oligomers. Several different molecular weights were simulated using the Bond Fluctuation Monte Carlo technique on a 20 x 20 x 20 unit lattice with periodic boundary conditions. After a monodisperse "melt" was equilibrated, chain ends were linked whenever they came within the allowed bond distance. Ends remained reactive throughout, so that multiple links were permitted. Even under these very liberal crosslinking assumptions, geometrical factors limited the degree of crosslinking. Average crosslink functionalities were 2.3 to 2.6; surprisingly, they did not depend strongly on the chain length. These results agreed well with the degrees of crosslinking inferred from experiment in a cured phenylethynyl-terminated polyimide oligomer.			
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